⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 260 870**
**A2**

## ⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **87307965.1**

(51) Int. Cl.⁴: **H01F 1/06** , H01F 1/08

㉒ Date of filing: **09.09.87**

㉚ Priority: **12.09.86 US 906819**

㊸ Date of publication of application:
**23.03.88 Bulletin 88/12**

(84) Designated Contracting States:
**DE FR GB IT NL**

(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
**3M Center, P.O. Box 33427**
**St. Paul, Minnesota 55133-3427(US)**

(72) Inventor: **Hopstock,David M.**
**c/o Minnesota Mi.&Ma.Cie 2501 Hudson Road**
**St, Paul, Minnesota 55133(US)**

(74) Representative: **Baillie, Iain Cameron et al**
**c/o Ladas & Parry Isartorplatz 5**
**D-8000 München 2(DE)**

# ㊹ Polymeric bonded metal magnet with corrosion resistant metal particles.

㊼ A highly stable, non-pyrophoric, highly corrosion resistant magnetic powder provided by treating magnetic particles with a solution containing chromate or dichromate ions and polymeric magnets containing the powder.

# POLYMER BONDED METAL MAGNET WITH CORROSION RESISTANT METAL PARTICLES

## Technical Field

This invention realtes to non-pyrophoric corrosion resistant magnetic metal particles and more particularly to a polymer bonded magnet with non-pyrophoric, corrosion resistant metal particles.

## Background of the Invention

Polymer bonded metal magnets are recognized to have a number of advantages over sintered or cast metal magnets. Magnetic articles can be molded to precise specifications, eliminating costly finishing steps, such as grinding. The polymeric bonding process provides a more uniform distribution of magnetic moment throughout the magnet and provides less variation between individual magnets. Polymeric magnets are less susceptible to damage during handling, such as chipping or cracking.

If desired, the polymeric magnets can be machined with conventional equipment such as lathes and drills, which equipment generally can not be used with the hard and brittle, cast or sintered magnets. By use of an elastomeric binder, polymeric magnets can be produced in a flexible form for ease of workability. For example, a polymeric magnet can be cut with a knife and fit easily inside a motor housing.

The size of the metal particles used is dependent on the method of fabrication. The average particle size ranges from 0.1 to 1000 microns, and is typically between 2 to 200 microns. The desired particle size is generally produced by grinding. However, grinding creates a severe oxidation problem. The most severe oxidation problems occur with rare earth metal magnet powders, such as samarium-cobalt (SmCo) and neodymium-iron-boron (NdFeB).

Oxidation can occur at various times during the production and use of bonded magnets. If rare earth metal powders are ground dry in air, very rapid oxidation, leading to fire and explosion, can occur. Alternatives to dry grinding in air include grinding in an inert gaseous atmosphere or in an inert liquid. These alternatives have high production costs while still providing a powder that may oxidize rapidly when exposed to air.

The powder is also susceptible to corrosion via oxidation during storage prior to being mixed with polymer. Also, oxidation is of particular concern during the process of compounding the magnetic powder with the polymeric binder. Mixing to form injection molding compounds typically takes place at temperatures between 190°C and 350°C. Although attempts have been made to compound in an inert gas, it is not possible to completely exclude all oxygen, which may be adsorbed on the particles and be present in the polymer.

Further oxidation may take place during the injection molding process, typically carried out at from 230°C to 350°C. For flexible magnets, oxidation is most likely to occur during the process of curing the elastomer. The finished magnets are subject to a gradual process of corrosion of the metal particles, which is accelerated by exposure to increased heat or humidity, as all organic polymers allow at least a small amount of oxygen and moisture to diffuse therethrough.

The prior art attempts at solving the above-identified problems can be put into two categories. (A), methods in which the individual metal particles are protected, and (B), those in which only the finished magnet is protected, usually by some type of exterior coating, such as an anticorrosive paint. In comparison to category A, methods of category B have two major disadvantages: (1) the particles are not protected during the earlier stages of fabrication of the magnet, and (2) the addition of a protective coating, which is generally several mils thick, makes it difficult to meet exacting dimensional tolerances in the finished product.

Category A attempts have also fallen short. As the magnetic particles themselves are typically only a few microns in diameter and maximum loading of magnetic material in the matrix is desired, the protective coating must typically be less than 0.1 micron thick. Various metal coatings, such as nickel, tin, zinc, and silver, can be produced by electroless plating, vapor deposition, and other methods. However, the metal coating methods are relatively expensive and subject to rapid failure from pinholes, uneven deposition, or other defects. Treatment with silane and titanate coupling agents has been reported to give a modest increase in surface stability. Treatment with phosphorus compounds has been proposed in relation to SmCo (U.S. Patent 4,497,722) and NdFeB (Japanese Patent Appl. 85-240,105 and European Patent Appl. 166,597). Similarly, treatment with organic dyes, such as C.I. Solvent Black 7, has been proposed in relation to SmCo (U.S. Patent 4,543,382) and NdFeB (Japanese Patent Appl. 85-242-604).

U.S. Patent No. 3,932,293 (the '293 patent) teaches the use of chromium-based treatment of iron, cobalt and nickel particles used in magnetic recording media. However, at col. 2 lines 6-8 the patent states that the pyrophoricity of the particles is apparently not improved by the treatment taught. Thus when exposed to air the particles treated by the '293 patent apparently are still susceptible to fire or explosion.

It is thus desirable to provide a metal magnet powder that is highly stable during all stages of manufacture of a polymer bonded metal magnet including being non-pyrophoric when exposed directly to air at elevated temperatures. It is also desirable that the metal powder be highly corrosion resistant and able to retain its magnetic properties under service conditions.

## Summary of the Invention

The present invention provides a highly stable, non-pyrophoric, highly corrosion resistant magnetic powder for use in polymer bonded metal magnets by providing magnetic particles treated with a solution containing chromate of dichromate ions or molecules having chromate functional groups. The magnetic particles are preferably rare earth magnetic metals. After drying in air the particles are non-pyrophoric and remain resistant to oxidation throughout the life of the magnet.

The non-pyrophoric permanent magnetic powder of the present invention comprises permanent magnet particles having an average particle size of from 0.1 to 1000 microns having a thin outer layer comprising a chromium and oxygen compound coated on said powder with the thin outer layer comprising between 0.001 and 5% by weight of the particles, preferably between 0.01 and 1%. The permanent magnetic particles preferably include a rare earth metal. The powder of the present invention is preferably sufficiently non-pyrophoric that it can be heated in air to 250°C without danger of fire or explosion.

The present invention also includes a polymeric magnet composition which comprises the above described powder bound in a binder selected from the group consisting of thermoplastics, thermosets, and elastomers.

The chromate treatment method as described above removes only a small fraction of the chromium from the treating solution. The present invention also contemplates several alternatives in which almost all of the remaining chromate is precipitated in an insoluble form on the surface of or admixed with the metal powder. One alternative involves adding a soluble salt that contains a cation that will precipitate an insoluble chromate. Examples include adding soluble zinc, cadmium, or lead salts to precipitate the insoluble chromates of those metals. These methods remove a large fraction of the remaining chromium from solution and improve the high temperature stability of the powder over that obtained with the standard chromate treatment.

Another method has been developed which gives better water quality than the metal chromate precipitation methods. A reducing agent, such as sodium bisulfite, is added to the metal powder-chromate solution slurry to reduce the chromium from the hexavalent chromate state to the trivalent chromic state. Base is then added to precipitate the chromium as a thin film of chromic hydroxide on the metal particles. After drying a very effective passivating layer is formed. The high temperature stability is significantly better than that produced by the standard chromate treatment. By proper choice of reagents and adjustment of conditions, almost all of the chromium is removed from solution and the effluent can be sent directly to a sewage treatment facility.

## Detailed Description

The present invention is applicable to all classes of permanent magnet alloy powders, including rare earth, Alnico (iron-aluminum-nickel-cobalt), manganese-aluminium, and others. It is particularly useful with the rare earth alloy magnet powders, including neodymium-iron-boron (NdFeB) and samarium cobalt (SmCo), since they have a very strong tendency to oxidize.

Production of polymer bonded magnets containing the stabilized powder can be by any of the large number of processing methods, including injection molding, compression molding, impregnation, extrusion, and calendering. Polymers used can include (1) thermoplastics, such as polyamides (nylons) and polyphenylene sulfide; (2) thermosets, such as epoxies and phenolics; and (3) elastomers, such as natural and synthetic rubbers and fluorocarbon elastomers. Other useful polymeric binders, such as polyesters, can be included in all three categories.

The chromate treatment can be conveniently applied by dissolving chromate salts, dichromate salts, chromium trioxide, or a mixture of these in water. Suitable salts include but are not limited to sodium dichromate, sodium chromate, potassium dichromate and potassium chromate. Alternatively, an organic compound containing hexavalent chromium in a functional group, dissolved in an appropriate solvent, may be used. In aqueous solution the following equilibria are rapidly established:

$CrO_3 + H_2O = HCrO_4^- + H^+$

$Cr_2O_7^{2-} + H_2O = 2\ HCrO_4^-$

$HCrO_4^- = H^+ + CrO_4^{2-}$

It can be seen that, regardless of the compounds that are used to make up the solution, the concentrations of the various species in solution are controlled by the pH and the total chromate concentration. The pH of the aqueous solution is preferably between 2.5 and 11.5. Use of a sodium or potassium dichromate solution typically gives an initial pH of 4 to 5, which is a particularly desirable range. The concentration of chromate can be from 0.1 percent by weight to the solubility limit, with 1 to 10 percent being a particularly desirable range. Although the details of the reaction mechanism are not known, it is believed that the chromate ion, which is a strong oxidizing agent, reacts with the metal surface by the half-cell reaction.

$CrO_4^{2-} + 4\ H_2O + 3\ e^- \rightarrow Cr\ (OH)_3 + 5\ OH^-$

As the reaction proceeds, the generation of hydroxyl ions increases the solution pH. Simultaneously, metal atoms at the surface are oxidized to metal ions. coprecipitating with the chromic hydroxide at the metal particle surfaces are hydroxides of the metal ions, such as $R(OH)_3$, where R is a rare earth metal, $Fe(OH)_2$, $Fe(OH)_3$, and $Co(OH)_2$. A gelatinous coating, which may also contain some chromate compounds, such as $CrOHCrO_4$ and $FeCrO_4$, forms at the surface of the metal particle. Upon drying the surface coating dehydrates and hardens to provide an effective barrier against further corrosion.

Before drying the particles, the soluble salts should be removed. Many techniques can be used, such as rinsing and decantation or running clear water through a filter or centrifuge cake. No sign of chromate coloration in the rinse water indicates an adequate rinse.

Drying can be carried out in an air circulating oven at temperatures from 60°C to 150°C. The higher drying temperature appears to give better resistance to corrosion in humid atmospheres.

A very effective method of applying the chromate treatment to the metal magnet powder is to grind the powder in an aqueous chromate solution. By this method the chromate can react with the surfaces of the particles as soon as they are formed, and thus corrosion during grinding is minimized. Grinding is preferably done with a ratio of volume of metal to be ground to total volume of slurry of between 0.10:1 and 0.50:1. On a weight basis, the percent solids in the slurry is preferably between 40 and 90 percent. However, grinding is not essential to the success of the chromate treatment. The treatment is also effective when applied to particles that have already been ground, provided significant oxidation of the particle surfaces has not already taken place.

The chromate treatment is conveniently and effectively done at room temperature, 20-25°C. The temperature of the slurry will rise during extended grinding. Temperatures of up to 50°C have been encountered with no deleterious effect on the chromate treatment process.

Although the chromate treatment process as described above is very effective there are two reasons why further treatment may be desired: (1) to further improve the corrosion resistance by precipitating a second layer of insoluble chromate onto the surfaces of the particles, and (2) to remove chromate from solution to facilitate disposing of the solution in an environmentally acceptable manner.

One effective method of further treatment is to add the soluble salt of the metal that forms an insoluble metal chromate. For example, zinc sulfate or zinc nitrate can be added to precipitate zinc chromate, or lead nitrate can be used to precipitate lead chromate. After the chromate treatement of the metal magnet powder is completed, a slight stoichiometric excess of the soluble salt is added to the metal powder/chromate solution slurry, either as a powder or as a solution, and stirred to mix thoroughly. It is generally desirable to subsequently adjust the pH to between 8 and 11 by adding a base such as sodium hydroxide or lime. The base facilitates complete precipitation of the metal chromate by converting $Cr_2O_7^{2-}$ and $HCrO_4^-$ to $CrO_4^{2-}$. The base also precipitates residual metal cations as the hydroxides in a mixture with the chromate. The actual precipitated species may in fact be a basic metal chromate, such as basic zinc chromate or basic lead chromate. Rinsing and drying are conducted as with the standard chromate treatment.

Another effective method of removing the chromate from the solution as a protective layer on the surfaces of the particles is by adding a reducing agent to convert the chromium from the hexavalent chromate state to the trivalent chromic state. Base is then added to precipitate the trivalent chromium as chromic hydroxide. Sodium bisulfite, $NaHSO_3$, was found to function effectively as a reductant. Other reductants commonly used to reduce chromium in water treatment, such as sulfur dioxide, sodium sulfite, sodium pyrosulfite or metabisulfite ($Na_2S_2O_5$), ferrous sulfate, and hydrazine, could also be used. Other reducing agents may also be substituted by one skilled in the art.

In the case of sodium bisulfite, the reduction reaction is essentially completed within 5 minutes at room temperature provided the pH is first reduced to between 3 and 3.5. Excessive addition of acid should be avoided, because the particles can be attacked by a solution more acidic than pH 3. Adjustment of pH can be done with hydrochloric, sulfuric, phosphoric or other suitable acids.

After the reduction reaction is completed, as indicated by a change from the yellow or orange color of the chromate to the deep green color of the chromic ions, base is added to precipitate chromic hydroxide. The desirable pH range is 8 to 11.5. Sodium hydroxide and lime are economical and effective bases, but other suitable bases can be substituted. In comparison to sodium hydroxide, lime gives somewhat better corrosion resistance and markedly better quality of the waste water. In most cases, after solid-liquid separation, the water is low enough in chromate content to be discharged directly to a sewage treatment plant. Again, rinsing and drying follow the procedure used for the standard chromate treatment.

The invention will now be illustrated by the following examples. In the following, all solution concentrations are expressed as percents, corresponding to grams of unhydrated solute per 100 grams of solution.

## Example 1

A 3.5 inch diameter by 4 inch deep attritor bowl was charged with 2000 grams of 3/16 inch diameter steel grinding balls. To the attritor were added 480 grams of minus-40-mesh "Magnequench" crushed NdFeB ribbon and 160 grams of the solution used to treat the powder. The slurry was ground for 20 minutes at 300 rpm. The initial temperature was 20°C; the temperature after grinding was approximately 35°C. The slurry was rinsed with tap water from the attritor into a flat-bottomed tray. The grinding balls were caught and rinsed on a screen. After 15-30 minutes were allowed for the particles to settle to the bottom of the tray, the solution was decanted. The tray was then refilled and the particles redispersed with more tap water. Again, after 15-30 minutes, the solution was decanted. This rinsing procedure was repeated once more to produce a clear supernatant. The wet powder was then dried in an air circulating oven at 60°C for approximately 15 hours, or until dry.

The stability of the powder with respect to oxidation was determined gravimetrically by heating in air. A 1-gram sample was weighed out into a tared crucible. The crucible was heated in air at 250°C for 1 hour. The crucible, after being allowed to cool to room temperature, was reweighed. This procedure was repeated on the same sample at 275, 300, and 325°C. A weight gain of more than 0.5 percent indicates that oxidation has proceeded to the point that significant loss in magnetic properties has occurred. A weight gain of more than 5 percent indicates that the powder is completely blackened and destroyed as a useful magnet material.

The following treatment solutions were used:

(1) control solution, pure tap water

(2) 3 percent solution of sodium dihydrogen phosphate

(3) a solution consisting of Amchem Products "Granodine 165SD" commercial phosphate treatment solution, diluted 66:1 with water

(4) solutions of sodium dichromate, at 0.1, 0.3, 1,0, 3.0, and 10.0 percent concentration.

The results of the heating tests are given in Table 1. It can be seen that the beneficial effect of chromate treatment becomes apparent at 1 percent concentration and increases as the concentration increases to 10 percent. Even at the 1 percent level, the chromate treatment is much more effective than the phosphate treatment, which is representative of the prior art.

TABLE 1. Results of high temperature tests on powders of Example 1.

| TREATMENT | PERCENT GAIN IN WEIGHT | | | |
|---|---|---|---|---|
| | 250 | 275 | 300 | 325°C |
| Control | 7.6 | 7.7 | 8.3 | 9.2 |
| $NaH_2PO_4$ | 0.6 | 5.3 | 6.5 | 7.7 |
| "Granodine 165 SD" | 6.6 | 6.8 | 7.4 | 8.3 |
| 0.1% $Na_2Cr_2O_7$ | 6.2 | 6.6 | 7.3 | 8.4 |
| 0.3% $Na_2Cr_2O_7$ | 6.6 | 6.9 | 7.7 | 8.7 |
| 1.0% $Na_2Cr_2O_7$ | 0.4 | 0.9 | 2.7 | 4.0 |
| 3.0% $Na_2Cr_2O_7$ | 0.3 | 0.6 | 2.2 | 6.1 |
| 10.0% $Na_2Cr_2O_7$ | 0.1 | 0.3 | 0.8 | 3.4 |

## Example 2

A 480-gram sample of "Magnequench" NdFeB ribbon was ground in 3 percent $Na_2Cr_2O_7$, following the procedure given in Example 1, except with a 15 minute grind time. Rinsing and drying as in Example 1 completed what was designated as treatment 2A. Treatment 2B began with the same grind procedure. After the slurry had been rinsed into the flat-bottomed tray, 12.64g of $ZnSO_4 \bullet 7H_2O$ powder was stirred into the slurry. A 10 percent solution of sodium hydroxide was added in increments with stirring to increase the pH of 8.0. A yellowish precipitate was observed to form. Rinsing and drying were as in Example 1. In treatment 2C the same procedure was used, but instead of the zinc salt, 14.56 g of $Pb(NO_3)_2$ powder were stirred into the slurry. The same pH adjustment, rinsing, and drying steps were used.

The results of the heating tests are given in Table 2. It is apparent that precipitation of zinc chromate and lead chromate in treatments B and C, respectively, gave better stability at 300°C than treatment A. Treatment C was marked more effective at 325°C.

TABLE 2. Results of high temperature tests on powders of Example 2.

| TREATMENT | PERCENT GAIN IN WEIGHT | | | |
|---|---|---|---|---|
| | 250 | 275 | 300 | 325°C |
| 4A | 0.1 | 0.2 | 1.2 | 4.3 |
| 4B | 0.0 | 0.2 | 0.7 | 5.7 |
| 4C | 0.0 | 0.3 | 0.6 | 1.3 |

## Example 3

A 4 x 2 factorial experiment was conducted in which the standard chromate treatment was followed by reduction of hexavalent chromium to the trivalent by sodium bisulfite and precipitation of chromic hydroxide. An attritor grind of "Magnequench" powder was done in 3 percent sodium dichromate, as in Example 1, with the grinding time extended to 40 minutes. After the ground slurry was rinsed from the balls, one of four treatments was performed. In three of the treatments, 10 percent solutions of hydrochloric, sulfuric, and phosphoric acid were added to adjust the pH of the slurry to 3. The fourth treatment was not to acidify the slurry. After each of the four treatments, 6.91g of sodium bisulfite were stirred into the slurry for 5 minutes.

The reduction was apparent in the appearance of the deep green color of the chromic ions. Chromic hydroxide was then precipitated by adjusting the pH to 8 by stirring in either 10 percent sodium hydroxide or powdered calcium oxide. After being allowed to stand for 30 minutes, the solution was decanted. Two further rinses and decants were done. The powder was then dried at 150°C for 2 hours.

For these samples a second test of corrosion resistance was conducted in addition to the high temperature stability test described in Example 1. A 2-gram sample was weighed into a small glass bottle. The small bottle was placed on a shelf in a larger sealed glass container commonly used as a desiccator. Underneath the shelf was a saturated solution of potassium chloride. This container, when placed in an oven held at 90°C, maintained a 75 percent relative humidity atmosphere. This method gives an accelerated test of corrosion under high humidity conditions. The extent of corrosion is conveniently determined gravimetrically. Again, a 0.5 percent weight gain indicates a significant deterioration in magnet properties. A control sample, ground for 20 minutes in water, gains 1.6 percent weight when held for 70 hours under this condition.

Table 3 gives results for weight gain after heating for one hour successively at 250, 275, and 300°C. Table 4 gives results for weight gain after exposure to 90°C and 75 percent relative humidity for 70 hours. It can be seen that the use of lime rather than sodium hydroxide for precipitation gave better corrosion prevention in almost every case. It also gave better clarity of the waste water. Acidifying the solution before adding the reductant gave improved results, presumably by promoting completion of the reduction reaction. Of the acids tested, phosphoric acid appears to give best corrosion resistance when incorporated into the chromate reduction-precipitation process.

TABLE 3. Results of high temperature tests on powders of Example 3.

| ACID | PERCENT GAIN IN WEIGHT<br>BASE USED FOR PRECIPITATION | |
|---|---|---|
| | NaOH | CaO |
| None | 0.9 | 1.1 |
| HCl | 1.0 | 0.6 |
| $H_2SO_4$ | 1.1 | 0.7 |
| $H_3PO_4$ | 0.9 | 0.6 |

TABLE 4. Results of high humidity and temperature tests on powders of Example 3.

| ACID | PERCENT GAIN IN WEIGHT<br>BASE USED FOR PRECIPITATION | |
|---|---|---|
| | NaOH | CaO |
| None | 1.3 | 0.6 |
| HCl | 0.8 | 0.4 |
| $H_2SO_4$ | 1.1 | 0.5 |
| $H_3PO_4$ | 0.3 | 0.0 |

Example 4

The minus-325-mesh size fraction was dry screened out for a sample of samarium-cobalt permanent magnet powder of the 2:17 precipitation hardened type. Treatment 4A was a control treatment that consisted of wetting a 1-gram sample of the powder with tap water for 10 minutes, decanting, and drying at 60°C. In treatment 4B, 1 gram of powder was wet with 0.25 gram of 3 percent sodium dichromate for 10 minutes. The sample was rinsed and decanted 3 times and dried at 60°C. In treatment 4C, the 10 minute sodium dichromate treatment was repeated. Then 0.36g of 3 percent sodium bisulfite was stirred in, and the pH was adjusted to 8.5 with saturated lime water. Rinsing and decanting was as in treatment 4B.

The results of high temperature tests as described in Example 1 are given in Table 5. It can be seen that the chromate treatment increased the oxidation resistance of the powder. Adding the chromate reduction-pricipitation process gave a further increase in oxidation resistance.

TABLE 5. Results of high temperature tests on powders of Example 4.

| TREATMENT | PERCENT GAIN IN WEIGHT | | | |
|---|---|---|---|---|
| | 250 | 275 | 300 | 325°C |
| None | 0.6 | 1.1 | 2.0 | 3.6 |
| 4A | 0.7 | 1.1 | 2.2 | 3.4 |
| 4B | 0.4 | 0.6 | 1.4 | 2.2 |
| 4C | 0.2 | 0.4 | 0.6 | 1.2 |

Example 5

To the attritor described in Example 1 were added 1840 grams of 3/16 inch diameter steel grinding balls, 240 grams of minus-40-mesh "Magnequench" crushed NdFeB ribbon, and 160 grams of 3 percent sodium dichromate solution. The powder was ground for 20 minutes at 300 rpm and then rinsed and dried as in Example 1. The following mixture was compounded in a laboratory Haake Buchler Rheomix mixer:

(a) 47.25 g of the powder prepared as described above

(b) 141.75 g of minus-100-mesh "Magnequench" crushed NdFeB ribbon

(c) 13.66 g of an essentially amorphous hot-melt polyamide resind, as described in U.S. Patent 4,200,547

(d) 0.86 g of a processing additive which is a cyclic nitrile derivative of a saturated fatty acid dimer, as described in the same patent.

Compounding was done at a temperature of 190°C for 6 minutes at 30 rpm, and an additional 4 minutes at 100 rpm.

The compound thus produced was injection molded on a laboratory machine to produce cylindrical pellets 0.47 inch in diameter and 0.30 inch thick. The temperature of the barrel and nozzle was 240-270°C, the temperature of the mold was 25-40°C, and the injection pressure was approximately 4000 psi. Orienting fields of 0 to 15 kOe were applied, but found to have no significant effect of the magnetic properties of samples made from the isotropic powder.

Table 6 gives the magnetic properties of the pellets as originally produced and after three different 9 month aging tests, at 90°C and ambient humidity, at 90°C and 75 percent relative humidity, and at 140°C and ambient humidity. All samples were pulsed magnetized at 40 kOe before measurement at 22°C on a Walker Hysteresisgraph. The magnetic properties given are defined by ASTM A340, with the exception of $H_x$, which is defined as the demagnetizing field that gives a 10 percent loss in induction upon recoil to zero demagnetizing field. Table 7 gives for the same aging conditions the percent change in weight, the percent change in magnetization in the open circuit condition, the percent change in magnetization in the closed circuit condition, and the percent change in magnetization in the closed circuit condition that is not recovered upon remagnetization. The latter corresponds to the loss of $B_r$ in Table 6 and is indicative of permanent metallurgical changes, such as corrosion, in the magnet.

The aging results at 90°C and ambient humidity indicate only a 4 percent loss in magnetization, all of which can be recovered by remagnetization. The molded magnet containing the stabilized powder is clearly suitable for continuous duty at 90°C. The 90°C, 75 percent relative humidity results indicates a small but significant degree of metallurgical change, probably related to corrosion. However, this is an accelerated test at a combination of high temperature and humidity rarely encountered in applications. The magnet is stable indefinitely under normally encountered high humidity conditions at temperatures up to 40°C. The 140°C results indicate that the magnet could be used in continuous service at that temperature if only exposed to weak demagnetizing fields. Overall, the results compare favorably with those reported for other bonded rare earth magnets.

TABLE 6. Magnetic properties of injection molded magnet of Example 5.

| | | After 9 months aging | | |
|---|---|---|---|---|
| | Original | 90°C | 90°C, 75%rh | 140°C |
| $B_r$ (kG) | 5.0 | 5.0 | 4.8 | 5.0 |
| $H_c$ (kOe) | 4.3 | 4.2 | 3.7 | 3.7 |
| $BH_{max}$ (MGOe) | 5.4 | 5.2 | 4.3 | 4.6 |
| $H_x$ (kOe) | 10.5 | 9.9 | 7.5 | 5.2 |
| $H_{ci}$ (kOe) | 13.5 | 13.2 | 12.4 | 10.7 |

TABLE 7. Effect on 9 month aging on properties of injection molded magnet of Example 5.

| | Percent Change | | |
|---|---|---|---|
| Property | 90° | 90°C,75%rh | 140°C |
| Weight | -0.1 | +0.5 | +0.3 |
| Open Circuit Magnetization | -4 | -15 | -13 |
| Closed Circuit Magnetization | -4 | -10 | -11 |
| After Remagnetization | 0 | -5 | 0 |

Example 6

A sample of the ground magnet powder prepared in the 4 x 2 factorial experiment of Example 3, with phosphoric acid used for pH adjustment and calcium oxide for chromic hydroxide precipitation, was used to prepare a flexible magnet product. The following mixture was compounded in a laboratory Haake Buchler Rheomix mixer:

(a) 240.00 g of the powder described above
(b) 15.00 g of medium acrylonitrile-butadiene rubber
(c) 0.15 g of stearic acid
(d) 0.09 g of tetramethylthiuram disulfide
(e) 0.18 g of sulfur
(f) 0.36 g of 2-mercaptobenzothiazyl disulfide
(g) 0.54 g of zinc oxide

Compounding was done for 3 minutes at 100 rpm, with the temperature rising from 60 to 110°C. The compound was allowed to cool to room temperature and then calendered into a 0.87 inch thickness sheet on a pair of 3 inch diameter by 9 inch long rolls. The sheet was cured for 40 minutes at 150°C in an air circulating oven.

The magnetic properties of the flexible sheet, determined with Walker Hysteresisgraph after pulse magnetizing at 40 kOe, were as follows:

$B_r$ = 4.5 kG
$H_c$ = 3.7 kOe
$BH_{max}$ = 4.1 MGOe
$H_{ci}$ = 15.1 kOe
$H_x$ = 8.0 kOe

The sheet had a tensile strength of 280 psi with an elongation of 53 percent (ASTM D412) and a Shore D hardness of 37. The high degree of flexibility of the sheet was evidenced by its ability to withstand a 180 degree bend around a 0.25 inch diameter mandrel without crazing.

## Claims

1. A non-pyrophoric permanent magnetic alloy powder comprising

(a) permanent magnetic alloy particles having an average particle size of from about 0.1 to about 1000 microns and

(b) a thin outer coating on said particles comprising a chromium and oxygen compound wherein the chromium content of said outer coating comprises between 0.001 and 5% by weight of the particles.

2. The powder of claim 1 wherein said permanent magnetic alloy particles include a rare earth metal.

3. The powder of claim 2 wherein said permanent magnetic alloy particles are selected from the group consisting of samarium-cobalt and neodymium-iron-boron.

4. The powder of claim 1 wherein the chromium content of said thin outer coating comprises between about .01% and 1.0% by weight of the particles.

5. The powder of claim 1 wherein said powder is sufficiently non-pyrophoric that it can be heated in air to 250°C without fire or explosion.

6. The powder of claim 1 wherein said thin outer coarting is formed by exposing said particles to a solution containing dichromate or chromate ions.

7. The powder of claim 6 further including adding a soluble metal salt capable of forming an insoluble metal chromate salt.

8. The powder of claim 7 wherein said insoluble metal chromate salt is selected from the group consisting of zinc chromate, cadmium chromate, and lead chromate or basic forms thereof.

9. The powder of claim 6 further including adding a reducing agent capable of reducing the chromium from the hexavalent chromate state to the trivalent chromic state and adding a base capable of precipitating chromic oxide, chromic hydroxide, or hydrated chromic oxide.

10. A polymeric magnetic composition comprising

(a) a binder selected from the group consisting of thermoplastics, thermosets, and elastomers; and

(b) a non-pyrophoric permanent magnetic alloy powder comprising a permanent magnetic particles and a thin outer coating on said articles comprising a chromium and oxygen composition wherein the chromium content of said outer coating comprises between 0.001 and 5% by weight of the particles.

11. The polymeric magnetic composition of claim 10 wherein said permanent magnetic alloy particles include a rare earth metal.

12. The polymeric magnetic composition of claim 11 wherein said permanent magnetic alloy particles are selected from the group consisting of samarium-cobalt and neodymium-iron-boron.

13. The polymeric magnetic composition of claim 10 wherein the chromium content of said thin outer coating comprises between about 0.01% and 1.0% by weight of said particles.

14. The polymeric magnetic composition of claim 10 wherein said binder is selected from the group consisting of polyamides, polyphenylene sulfide, epoxides, phenolics, natural rubbers, synthetic rubbers, fluorocarbons, and polyesters.

15. The polymeric magnetic composition of claim 10 wherein said particles have an average particle size of from about 0.1 to about 200 microns.

16. A method of treating magnetic particles comprising

a) grinding a permanent magnetic alloy in the presence of a solution containing a chromium compound selected from the group consisting of dichromate salts, chromate salts, chromium trioxide or mixtures thereof

b) separating the magnetic particles from the solution

c) drying the magnetic particles at a temperature of between 60°C and 150°C wherein a non-pyrophoric permanent magnetic alloy powder is produced having an average particle size between 0.1 and 200 microns and having a thin outer coating on said particles comprising a chromium and oxygen compound coated on said powder wherein the chromium content of said outer coating comprises between 0.001 and 5% by weight of the magnetic particles.

17. The method of claim 16 further including precipitating the remaining chromium in said solution by adding a soluble salt of a metal capable of forming an insoluble metal chromate.

18. The method of claim 17 wherein said soluble salt is selected from the group consisting of soluble salts of zinc, cadmium, and lead.

19. The method of claim 16 further including adding a reducing agent to the solution capable of converting the chromium from the hexavalent state to the trivalent state followed by adding a base to precipitate said trivalent chromium.

20. A compound capable of being used in an injection molding apparatus comprising a thermoplastic binder and a non-pyrophoric permanent magnetic alloy powder, said powder comprising

a) permanent magnetic alloy particles having an average particle size of between about 2 and about 200 microns,

b) a thin outer coating on said particles comprising a chromium and oxygen compound wherein the chromium content of said outer coating comprises bewteen 0.001 and 5% by weight of the particles.

21. A permanent magnet molded from the compound of claim 20.

22. A flexible magnet comprising a flexible thermoplastic or elastomeric binder and a non-pyrophoric permanent magnetic alloy powder, said powder comprising

a) a permanent magnetic alloy particle having an average particle size of between about 0.1 and about 50 microns; and

b) a thin outer coating on said particles comprising a chromium and oxygen compound wherein the chromium content of said outer coating comprises between 0.001 and 5% by weight of the particles.